ACIDIFICATION PROCESSES IN SOILS OF BISTRA
HIDROGRAPHIC BASIN

PROCESE DE ACIDIFIERE A SOLURILOR
DIN BAZINUL HIDROGRAFIC BISTRA

Nicoleta NEMEŞ

Politehnica University of Timisoara, Romania
Corresponding author: Nicoleta Nemeş, e-mail: nemesnicoletas@yahoo.com

Abstract: In this paper we studied the processes that generate acidity in the soils and the factors that determine it. For this we analysed a lot of pedological profile, a sample from Obreja and Glimboca, in Bistra Hydrographic Basin, Caraş-Severin County. From the pedological profile analyses we established that the acid soils, like luvosoils and districambosoils are predominant in the researches area and their acidity are determinate by the bases cations debasification and it forms a impermeable water horizon, Bt, that leads in time to oxide-reduction processes that will generate a soil acidification.

Rezumat: În această lucrare sunt studiate procesele care generează aciditate în soluri și factorii care le determină. Pentru aceasta au fost analizate un număr însemnat de profile pedologice, probe de sol preleveate de pe teritorial localităților Obreja și Glimboca, în bazinul hidrografic Bistra, județul Caraş-Severin. Din analiza profilelor pedologice studiate se constată că predomină categoria solurilor acide reprezente de luvosoluri și districambosoluri, aciditatea acestora fiind determinată de condițiile climatice din zonă, debazificarea cationilor bazici și formarea unui orizont argic, Bt, impermeabil pentru apă, ceea ce duce în timp, la procese de oxido-reducere care vor genera aciditate în sol.

Key words: acidity, pedological profile, soil sample, hydrographic basin, debasification, bases cations, oxide-reduction processes.

Cuvinte cheie: aciditate, profil pedologic, proba de sol, bazin hidrografic, debazificare, cationi bazici, procese de oxido-reducere

INTRODUCTION

Soil reaction affects the plants nutritive element absorption. A case, the essential cations absorption (Ca$^{2+}$, Mg$^{2+}$) is favoured by a neutral – low alkaline reaction medium, while the essential anions absorption (NO$^-_3$, SO$^{2-}_4$, H$_2$SO$^{4-}_4$) and microelements absorption take place in a acid reaction medium.

The soils acidity appears along with the debazification process, clay forming and migration. In fact, take place prime minerals debazification of adsorptive complexes and the place of basic cations are taken by hydrogen, aluminium and manganese ions.

The acid soils in our county were formed upon sedimentary rocks, with 600-900 mm/year precipitation, at 6-9°C medium annual temperature (Ianoş and Goian, 1997).

After the stock-taking made by Pedological and Agrochemical Researches Institute in Bucharest and by Pedological and Agrochemical Researches County Office, in our county the acid soils with agricultural using for that the amelioration is necessary covers 2.3 million ha, and the arable using covers 1.6 million ha (Soils Quality Monitoring, 1999).

In the west part of Romania the soils that have a moderate – excessive acidity covers more than 800 000 ha (Rogobete et al., 2000).

In acid soils class that needs amendments are included, generally, districambosoils, typical preluvosols, albic and typical luvosoils. At this soils are added the soils that are
anthropic acidity (by fertilisers, acid rains, pollution) in which the soil reaction are moved into the moderate and high acid domain and the aluminium becomes limiting factor.

MATERIAL AND METHOD

In this paper we present and discuss a series of acidification processes encountered in the soils of Bistra Hydrographical Basin, respectively in Obreja and G limboca locality. For this studies, classic physics and chemical analyse, mineralogical analyse of coarse material and loamy fraction analyse was performed.

RESULTS AND DISCUSSION

The more important sources of soils acidified processes from Bistra Hydrographical Basin area are:

Basics cations debasification and leakage;
Claying material and sesvioxide formation;
Deeping’s migration of colloidal particles forming an illuvial horizon B, impermeable for water;
Aluminium and iron sesvioxide decomposition and deposition.

In the soils that are affected by the erosion the $H_3O^+/HO^-$ rapport is favourable to hydrogen ions, the debasification are permanently and it is followed by a basic cations substitution by the ions that generated acidity ($H_3O^+$. $Al^{3+}$).

The hydrogen ions that generate the soils acidity are favoured for irreversible or partially reversible processes that take place in the soils. Along with the high chemical activity of hydrogen ions, in the low pH value ($pH < 5$), the aluminium and iron cations interact negatively and phytotoxic. These cations attend the change positions for the radicular system cations, disturb their absorption, and block the chemism and the nutrition with other elements (the more important effect is observed to phosphorus nutrition due to the immobilisation of this element) (Rusu et al. 2005).

In soil, at a pH level higher than the isoelectric point ($pH$ 6-6.5, in function of clay type), electric negative charge appear that rise from specific hydroxyl group dissociation ($SiOH$, $AlOH$) to the surface of mineral clay crystals.

The hypotheses regarding the soils acidification permit the explanation of acidity forms that native exist in the soils or that are developed throw the anthropic intervention or due to the acidity generation substances.

So, the easier changeable acidity, at 5.8-6.0 pH, is determined by the changeable aluminium ions and in smaller measure by the carboxylic functional groups of the soil’s organic mater.

The soils with a pH value bigger than 5.8-6.0 has a hard changeable potential acidity generated by the carboxylic groups of humic substances. (Rusu et al. 2005)

\[ RCOOH \leftrightarrow RCOO^- + H^+ \]  \[1\]

At this potential acidity form and in this pH range makes contribution, by hydrolyses way, the aluminium and iron basic salts:

\[ Al(OH)_2 \cdot H_2PO_4 + HOH \leftrightarrow Al(OH)_3 + H_2PO_4^- + H^+ \]  \[2\]

\[ Fe(OH)_2 \cdot H_2PO_4 + HOH \leftrightarrow Fe(OH)_3 + H_2PO_4^- + H^+ \]  \[3\]
At pH value between 6.5 and 9.0 the hydrogen ions come to the phenol groups of organic matters and to the polybasic radicals that are dissociated.

\[ R - C_6H_4OH \rightleftharpoons R - C_6H_4O^- + H^+ \]  

[4]

In the soils with pH value > 9.0, the hydrogen ions come to the unaromatic alcohols of the organic matter, to the acid carbonate and to the orthophosphates.

In the most of the cases, the aluminium excess and their toxic activity are attended by the toxicity of manganese and iron ions. These cations are less active action in the cation changes blocked position than the aluminium ions.

In the case of acid soils the relation between pH and Al\(^{3+}\) is essential, due to the fact that the bigger is the acidity; the aluminium ions generate a bigger acidity and becomes phytotoxic (Rusu et al. 2005).

\[ [\text{Al}(H_2O)_6]^{3+} + H_2O \rightarrow [\text{Al}(H_2O)_5(OH)]^{3+} + H_3O^+ \]  

[5]

These soils present, in the same time, a debasification processes with a base saturation degree (V\%) that shown that the advance acidification are attended by a debasification in the same manure.

The aluminium phytotoxic effects are founded in the plants radicular system weak grown. These effects are reduced, or inexistent at a pH value bigger than 5.8-6.0 when the mobile aluminium concentration are reduces under the value of 0.3 me/100 g soil, or under the value of 1.5-2.0 mg/100 g soil (Rusu et al., 2005).

The high basic cations concentration (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\)) that exceed the Al\(^{3+}\) concentration can attenuate the aluminium concentration. The same effect has the high phosphates contents (H\(_2\)PO\(_4^{-}\), HPO\(_4^{2-}\), and PO\(_4^{3-}\)) that reduce the aluminium toxicity due to the precipitations phenomena with aluminium phosphates formation (at the root surface or inside the roots), under this type of reaction:

\[ \text{Fe(OH)}_3 + H_3PO_4 \rightarrow \text{FePO}_4 + 3H_2O \]  

[6]

\[ \text{Al(OH)}_3 + H_3PO_4 \rightarrow \text{AlPO}_4 + 3H_2O \]  

[7]

For these reasons, is evident that a high content of Al\(^{3+}\) deteriorate the phosphate nutrition due to the fact that the monophosphate ions has a low activity because of aluminium excess ions. So, in more of the cases, the aluminium phytotoxicity are concluded with phosphorus deficiency.

Along with soils debasification and aerobics condition persistence, the tendency of Fe\(^{3+}\) ions accumulation exist, and the oxidation of these ions generate soil’s acidity (Rogobete, 2006).

\[ \text{Fe}^{2+} - \text{coloid} \rightarrow \text{Fe(OH)}_3 + 2H^+ - \text{coloid} \]  

[8]

The soils acidification processes by the iron ions reducing and oxidation alternation are named ferolyses. In anaerobic conditions, the Fe\(^{3+}\) ions are transformed in Fe\(^{2+}\) ions, that takes out the bases from the colloids surface and determinate their accumulation in the soils. In
the arid periods of the year, the bivalent iron ions are oxidised and at the colloids surface the hydrogen ions remain generating acid soils (Rogobete, 2006). The accumulation of acidity in the surface soil by ferrolysis is a localized process enabled by the spatial separation of acid-generating Fe\(^{2+}\) from the alkaline bicarbonate iron. It occurs only where drainage permits bicarbonate to leach through the soil profile. During wet periods, iron oxides undergo reduction, with organic matter supplying the electrons. The Fe\(^{2+}\) ions may then occupy a significant fraction of exchange sites on the soil colloids, like clays and humus.

Analytical dates for some pedological profile analysed to the area of Obreja and Glimboca in Caraș Severin County.

Table 1

<table>
<thead>
<tr>
<th>HORIZON</th>
<th>Ea</th>
<th>E/Ba</th>
<th>BtBa</th>
<th>B/Cg</th>
<th>Cg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (cm)</td>
<td>0.22</td>
<td>22.38</td>
<td>38.88</td>
<td>88.114</td>
<td>114.125</td>
</tr>
<tr>
<td>Mobil P (ppm)</td>
<td>12.2</td>
<td>8.7</td>
<td>5.4</td>
<td>6.7</td>
<td>6.7</td>
</tr>
<tr>
<td>Coarse sand (2.0-0.2 mm) %</td>
<td>6.0</td>
<td>7.6</td>
<td>2.9</td>
<td>1.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Fine sand (0.2-0.02 mm) %</td>
<td>33.0</td>
<td>30.3</td>
<td>31.6</td>
<td>29.1</td>
<td>30.7</td>
</tr>
<tr>
<td>Silt (0.02-0.002 mm) %</td>
<td>29.5</td>
<td>28.5</td>
<td>29.2</td>
<td>25.7</td>
<td>23.5</td>
</tr>
<tr>
<td>Clay (sub 0.002 mm) %</td>
<td>31.5</td>
<td>33.6</td>
<td>36.3</td>
<td>43.8</td>
<td>43.6</td>
</tr>
<tr>
<td>Physic clay (sub 0.01 mm) %</td>
<td>50.4</td>
<td>51.4</td>
<td>50.4</td>
<td>58.5</td>
<td>55.7</td>
</tr>
<tr>
<td>pH (H(_2)O)</td>
<td>5.40</td>
<td>5.15</td>
<td>5.55</td>
<td>5.90</td>
<td>6.10</td>
</tr>
<tr>
<td>Humus (%)</td>
<td>2.61</td>
<td>2.05</td>
<td>1.67</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>T (me)</td>
<td>18.44</td>
<td>18.70</td>
<td>15.97</td>
<td>25.20</td>
<td>25.55</td>
</tr>
<tr>
<td>V (%)</td>
<td>57.48</td>
<td>54.43</td>
<td>61.89</td>
<td>72.61</td>
<td>74.12</td>
</tr>
<tr>
<td>Al mobile (me/100g soil)</td>
<td>0.64</td>
<td>0.94</td>
<td>0.68</td>
<td>0.79</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>HORIZON</th>
<th>A(_w)</th>
<th>Ea</th>
<th>EB</th>
<th>BtBa</th>
<th>BCw</th>
<th>Cw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (cm)</td>
<td>0.20</td>
<td>20.35</td>
<td>35.67</td>
<td>67.88</td>
<td>88.110</td>
<td>110.170</td>
</tr>
<tr>
<td>Mobil P (ppm)</td>
<td>8.0</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
<td>10.8</td>
</tr>
<tr>
<td>Coarse sand (2.0-0.2 mm) %</td>
<td>2.6</td>
<td>4.0</td>
<td>2.7</td>
<td>2.1</td>
<td>3.6</td>
<td>2.8</td>
</tr>
<tr>
<td>Fine sand (0.2-0.02 mm) %</td>
<td>35.1</td>
<td>35.9</td>
<td>33.6</td>
<td>33.0</td>
<td>30.2</td>
<td>32.9</td>
</tr>
<tr>
<td>Silt (0.02-0.002 mm) %</td>
<td>42.0</td>
<td>37.2</td>
<td>35.3</td>
<td>36.1</td>
<td>30.6</td>
<td>30.0</td>
</tr>
<tr>
<td>Clay (sub 0.002 mm) %</td>
<td>20.3</td>
<td>22.9</td>
<td>28.4</td>
<td>38.8</td>
<td>35.6</td>
<td>34.3</td>
</tr>
<tr>
<td>Physic clay (sub 0.01 mm) %</td>
<td>41.5</td>
<td>42.1</td>
<td>46.3</td>
<td>59.8</td>
<td>53.3</td>
<td>51.1</td>
</tr>
<tr>
<td>pH (H(_2)O)</td>
<td>4.50</td>
<td>5.10</td>
<td>5.40</td>
<td>5.60</td>
<td>5.95</td>
<td>6.55</td>
</tr>
<tr>
<td>Humus (%)</td>
<td>2.68</td>
<td>1.80</td>
<td>1.43</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T (me)</td>
<td>12.10</td>
<td>13.31</td>
<td>17.06</td>
<td>20.59</td>
<td>25.27</td>
<td>28.03</td>
</tr>
<tr>
<td>V (%)</td>
<td>57.10</td>
<td>59.81</td>
<td>57.67</td>
<td>67.31</td>
<td>80.80</td>
<td>87.26</td>
</tr>
<tr>
<td>Al mobile (me/100g soil)</td>
<td>2.12</td>
<td>2.16</td>
<td>2.00</td>
<td>1.58</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Due to an insufficient base saturation and due to the acid medium (pH between 4.5-6.55), a migration of clay fraction from surface layer appear and result an impermeable horizon with a high content of clay, Bt horizon (with a medium clay contents of 47.33%). The strong and moderate acid reaction in association with high mobile aluminium content (value between 0.61-2.16 me/100 g soil), as much as the chemical, physical and biological characteristics, limited the soils production capacity and reduce the used fertilisers efficiency.
Beside the decrease of production, the more acid soils reaction induces a perturbation in the nutritive supply capacity. The major of acid soils are low or very low mobile phosphorus assurance and the fertilisers that include phosphorus are rapidly retrograded in other forms less accessible for the plants.

From the date analyses, as much as to other 102 pedological profile from the studied area, a 62.6% of agricultural soils, with a low and very low level of phosphorus (under 18 ppm mobile P) results. Regarding the arable soils, these states of fact are on more than 50% of researched area.

CONCLUSIONS

The anions adsorption capacity increases with the pH increase because the acidification processes increase the basic group’s capacity to accept the protons and, in so way, the anions electrostatic retention increase.

For the most part the phytotoxic effects, at very acid level of reactions, are refereed only to aluminium ions.

All the soils attribute (the reaction, the aluminium ions contents, the soluble salts, the texture, and the humidity), that influence in the soils the phosphates ions sorption-desorption-diffusion reactions, the phosphates insufficiency appears.

The aluminium and iron mobile forms are a toxic effect in the acid soils with pH lower than 6.0 (in water suspension). These type of soils have base saturation degree (V%) lower than 80%, in the case of soil with low texture, loamy and sand clay, and a pH value lower than 5.8.

The acid soils have a weak nutrients provision and their accessibility for plants is suppressed by the soils acidity and the aluminium ions.

REFERENCES

5. x x x - Monitoringul calității solurilor, 1999.